



Short Communication

Heat of reaction measurements for hydrothermal carbonization of biomass

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ABSTRACT

This paper presents a set of calorimetric measurements with the aim of better understanding the calorific nature of hydrothermal carbonization. Presented values so far show an inadequately high scatter to do so, preventing a well funded assessment of the energetic feasibility of this process.

The heat released during hydrothermal carbonization at 240 °C measured with the applied differential calorimetry setup is $-1.06 \text{ MJ/kg}_{\text{glucose,daf}}$ with a standard deviation of 14%, $-1.07 \text{ MJ/kg}_{\text{cellulose,daf}}$ with a standard deviation of 9%, and $-0.76 \text{ MJ/kg}_{\text{wood,daf}}$ with a standard deviation of 32%. These results are in good agreement with the theoretically derived maximum heat release. Despite the comparably high experimental standard deviation of these results, their accuracy is considerably higher than previously published results.

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1. Introduction

In the past decades, hydrothermal processes for the conversion of biomass have been mainly under consideration to produce liquids and/or product gas (Peterson et al., 2008). In addition to these processes, hydrothermal carbonization of biomass is attracting renewed interest (Cao et al., 2011; Inoue et al., 2002; Kumar et al., 2011; Lynam et al., 2011; Ramke et al., 2010; Titirici and Antonietti, 2010; Wittmann, 2010; Yan et al., 2010). In this process, biomass waste with a low calorific value and high water content can be upgraded to a solid, lignite-like fuel by applying comparably mild reaction conditions, typically around 200 °C under saturation pressure for several hours. Due to the improved handling properties of the product coal (stability, storage, friability), hydrothermal carbonization can help to increase the energetic use of biomass waste. Additionally, hydrothermal conditions open up a chemistry which has the potential to create solid products of high value (Libra et al., 2011; Titirici and Antonietti, 2010).

The investigation and discussion of biomass conversion processes for the production of fuels always has to include considerations of their energetic efficiency. Due to the fact that a comparably large amount of water is being heated, the auxiliary energy required to run the process becomes a decisive parameter especially for hydrothermal processes. It is mandatory to recover heat internally in order to achieve a viable biomass conversion (Peterson et al., 2008).

Next to this fundamental importance of heat recovery, there may also be a significant impact of the heat of reaction of hydro-

thermal carbonization. Reported values for this heat of reaction range from around zero up to $-5.8 \text{ MJ/kg}_{\text{feed,dry}}$ (see supplementary information). This range means that either external energy is required to sustain this conversion process or that enough energy can be recovered from this heat of reaction to heat up fresh water while still having energy left for other uses (e.g. drying of the product). In order to be able to evaluate the feasibility of hydrothermal carbonization, this range of uncertainty is insufficient. The aim of this paper is to present experimental investigations on this heat of reaction and reduce the scatter of reported values to a better defined quantity.

In addition, experiments have been performed to investigate the influence of temperature, solids loading, and acids. The impact of a variety of different acids and bases on the elemental composition of the produced coal has been investigated earlier (Funasaka and Yokokawa, 1951), but information on the impact on reaction kinetics is scarce. For this investigation, acetic, formic, and levulinic acid have been used because they are byproducts and thus might act as autocatalysts (Kuster, 1990; Yan et al., 2010).

2. Experimental

A power compensated differential scanning calorimeter from PerkinElmer (DSC-7) with stainless steel high pressure capsules has been used for the calorimetric measurements. The preparation, conduction, and evaluation of all experiments followed ISO 11357-1:1997 and ISO 11357-5:1999 using the isothermal method (test runs with temperature scans could not achieve reproducible results). Each test run was conducted with the nominal temperature being held for 10 h to assure a completed reaction (the reaction time was expected to be between 4 and 6 h). The reference capsule

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was filled with the same mass of distilled water as the sample mass. The tightness of both the reference and sample capsule was checked after each run by a determination of the weight difference. The cooler temperature was held at 20 °C by a thermostat/kryostat (Lauda RC6CS). The nitrogen purge gas flow was set at 1.3 bar.

Glucose, microcrystalline cellulose powder, and wood have been used as feed. Wood chips from poplar wood (*Populus Tremula*) have been grinded with a ball mill and the fraction with a particle size of <1 mm used for the experiments. All other chemicals were purchased as standard grade chemicals from Carl Roth GmbH + Co. KG (glucose, cellulose, indium and zinc for calibration, all acids used).

To determine the heat of reaction, reference conditions have been set at 240 °C and a solids loading of 20% (which is recognized as a lower limit for the feasibility of hydrothermal processes (Peterson et al., 2008)) in distilled water. Six runs have been performed at these reference conditions for each feed. Further experiments have been conducted to investigate the change of reaction conditions. For each variable changed, three runs have been performed.

The typical amount of reactants used was around 4 mg due to the size of the pressure capsules (30 µl). The time in between sample preparation and start of the experiment was <5 min.

The determination of the water content of the feed was conducted according to the oven dry method of DIN CEN/TS 14774–1:2004 (the sample was dried at 105 °C until stability of the mass was reached). This water content was assumed to be constant, because the laboratory was air-conditioned to meet reference conditions (20 °C, relative humidity ϕ = 40%; this assumption has been checked by repeated determination of the water content at a later stage of the experiments).

The method for the evaluation of the results has been presented and discussed in detail elsewhere (Funke and Ziegler, 2011).

3. Results and discussion

Results from measured heats of reaction are summarized in Table 1. They deviate significantly from most of the values published in literature. The following discussion will investigate this discrepancy in detail.

There have been two publications reporting a slightly endothermic heat of reaction which could also report a defined uncertainty (Sunner, 1961; Yan et al., 2010). However, only a very short residence time of several minutes has been applied. Theoretically, it can be expected that the reaction becomes exothermic for more severe reaction conditions, i. e. higher temperature and longer residence time. At such conditions, the product coal tends to carbonize more strongly, which is expressed by a further decrease of its atomic ratios H/C and O/C. The principal sum reactions effecting the elemental composition of the biomass during hydrothermal carbonization are dehydration and – to a lesser extent – decarbox-

ylation¹ (Funke and Ziegler, 2010), both of which exhibit a negative heat of reaction. Hence, the amount of energy released must progressively increase with stronger carbonization which explains the exothermic heat of reaction measured here (see Table 1).

The publications where more severe reaction conditions were applied (>200 °C, >1 h) reported a heat of reaction 100–600% higher than the obtained values from herein presented calorimetric measurements. Most of them were estimated by an energy balance of the feed and the solid product (coal). However, there are numerous organic byproducts in the product water (Gerhardt et al., 2010; Yan et al., 2010). Depending on the process conditions, minor amounts of combustible gases can be formed, too (Ramke et al., 2010). Neglecting these contributions to the energy balance can lead to an error of 100–600% (see supplementary information). This approximation cannot be regarded reliable unless all product fractions are being considered (as performed by Yan et al. (2010)).

Another approach to estimate the heat of reaction of hydrothermal carbonization was to derive a theoretical gross reaction equation and apply Hess's law (see supplementary information). In order to be able to determine the stoichiometric coefficients, only the solid product coal, water and carbon dioxide can be considered. Therefore it estimates a theoretical upper bound of the heat released during hydrothermal carbonization, which is $-2.4 \text{ MJ/kg}_{\text{reactant, dry}}$ for comparably severe reaction conditions (310–340 °C, 64–72 h; see also supplementary information) including the uncertainty for calculating the heating values with an empiric equation. The measured values presented in Table 1 are consistent with this theoretic derivation because less heat must be released in practice due to the inevitable occurrence of organic byproducts in the product water (and, depending on the process conditions, the production of combustible gases).

These theoretic considerations in conjunction with the performed calorimetric measurements lead to the conclusion that most published values overestimate the heat of reaction of hydrothermal carbonization significantly by 100–500%. In consequence, it cannot be expected that substantial amounts of heat energy will be available externally. Depending on the design, it might even be necessary to add some heat energy in order to run this process (Stemann and Ziegler, 2011). This fact represents an important factor in the assessment of this conversion technology, especially in comparison with other technologies such as e.g. pyrolysis or (hydrothermal) gasification. Notably, wood (i.e. actual biomass) releases even less heat than both glucose and cellulose. Under the given reaction conditions this corresponds in principal to ongoing dehydration and/or decarboxylation, which results in a stronger carbonization (i.e. the atomic ratios H/C and O/C of the produced coal decrease further). This fact is well known and can be attributed to lignin, which is carbonized less under hydrothermal conditions than cellulose (Funke and Ziegler, 2010).

The observed length of the heat effects is below the expected reaction time. However, it should be stated that this does not necessarily correspond to an end of reactions, but rather represents the end of detectable heat effects with the given precision of the experimental setup. The investigated feeds show characteristic differences in the development of heat over time (see Fig. 1). For the case of glucose and wood the majority of the heat is released within 30–40 min while it takes longer for (crystalline) cellulose, indicating slower reaction kinetics. Other observations can only be discussed with further analyses due to the limited suitability of differential calorimetry to assess the nature of reactions.

As expected, temperature has a strong influence on the kinetics of the reaction (see Fig. 2), but not on the quantity of the heat re-

Table 1

Experimental results for the heat of reaction of hydrothermal carbonization using a power compensated differential scanning calorimeter (ref: reference conditions at 240 °C, solids loading of 20%, pH 7).

Feed	Heat of reaction [MJ/kg _{daf}]	Standard deviation [MJ/kg _{daf}]	Mean peak length [min]
Glucose (ref)	−1.06	0.16	190
Cellulose (ref)	−1.07	0.11	210
Wood (ref)	−0.76	0.27	210
Cellulose (at 260 °C)	−1.08	0.08	210
Cellulose (with Acetic Acid, pH3)	−0.86	0.02	200

¹ It should be noted that decarboxylation of organic acids is not the only reaction mechanism that leads to the development of CO₂ in hydrothermal carbonization (Funke and Ziegler, 2010 and references therein).

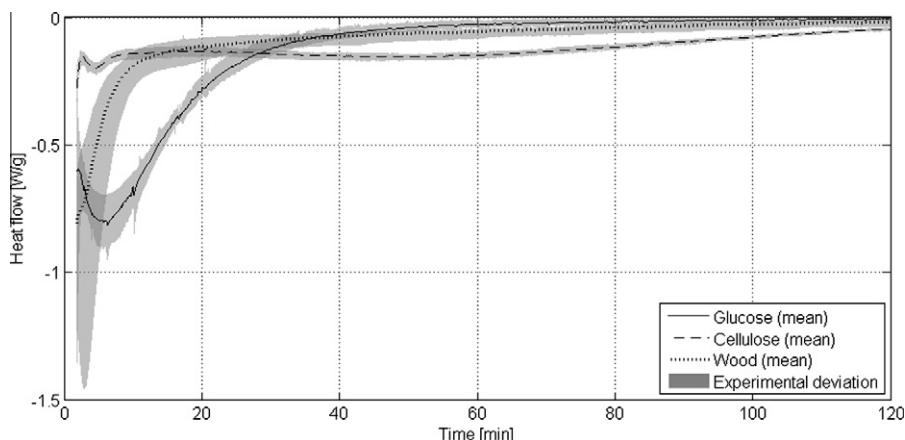


Fig. 1. Comparison of the results from hydrothermal carbonization of glucose, cellulose, and wood at reference conditions (240 °C, solids loading 20%, pH 7). Only the timeframe of 0–120 min is shown to enhance the clarity of the figure. The actual measurement lasted 600 min.

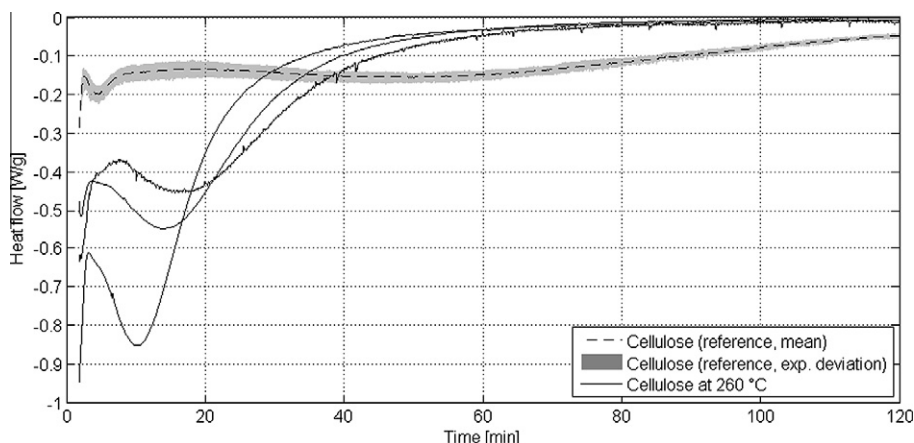


Fig. 2. Comparison of the results from hydrothermal carbonization of cellulose at 260 °C to the reference conditions (240 °C, solids loading 20%, pH 7). Only the timeframe of 0–120 min is shown to enhance the clarity of the figure. The actual measurement lasted 600 min.

leased. At a reaction temperature of 260 °C the heat released does not deviate statistically significant from the reference conditions (confidence interval <50%). It can be concluded that the heat effects are finished before the end of the measurement in both cases. This is of fundamental importance to the precision of the experimental procedure.

The solids loading did not show any effects on reaction kinetics in the range of 20–50% (see supplementary information).

The addition of acetic acid does not lead to a qualitatively different characteristic of the heat release (see Fig. 3). However, the amount of heat released is slightly lower than that of the reference conditions (with a confidence interval of about 95%). The application of other acids did not lead to any change in the characteristics of the heat release, too (see supplementary information). Based on these results it can be concluded that autocatalysis by the produced organic acids is very unlikely unless the pH drops below 3 (which has not been reported yet to the best knowledge of the authors). This is supported by previous findings which state that acidic hydrolysis takes place below a pH of 3 (Bobleter, 1994).

In general, the experimental setup exhibits a comparably high standard deviation for state of the art differential calorimetry. As discussed in detail elsewhere (Funke and Ziegler, 2011), this is mainly due to the use of the pressure capsules and the hydrothermal conditions, both of which add an undesirable thermal mass to

the measurement system. However, as this contribution of the thermal mass cannot be avoided by concept and the result is more precise than any other measurement of the heat of reaction of hydrothermal carbonization known to the authors, this uncertainty was accepted. It should be pointed out that the increase in uncertainty for the case of wood compared to glucose and cellulose must be attributed to the inhomogeneity of the biomass itself.

4. Conclusions

From a critical review and theoretic considerations it was concluded that no more than $-2.4 \text{ MJ/kg}_{\text{cellulose}}$ heat can be released during hydrothermal carbonization at a comparably strong carbonization. Presented experimental results were less than half as high as this theoretically derived value, i.e. $-1.07 \text{ MJ/kg}_{\text{cellulose}}$ and $-0.76 \text{ MJ/kg}_{\text{wood}}$. The kinetics of the heat effects was not affected by added acetic and formic acid at a pH of 3. Therefore, autocatalysis of this reaction appears unlikely if the pH remains above 3 during hydrothermal carbonization.

In contrast to previous findings, these new results indicate that the heat of reaction will have a minor influence on the overall energy balance of this conversion process, especially compared to the heating of the water. However, it is strongly emphasized that this energy release cannot be neglected regarding safety issues.

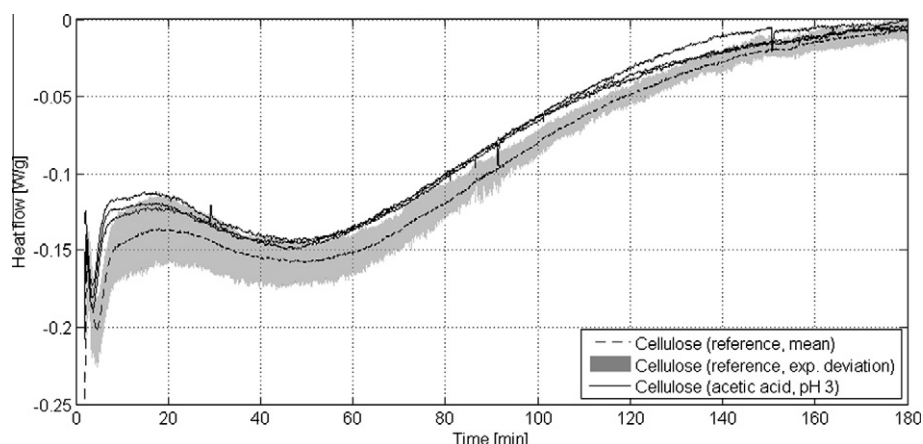


Fig. 3. Comparison of the results from hydrothermal carbonization of cellulose with acetic acid (pH 3) to the reference conditions (240 °C, solids loading 20%, pH 7). Only the timeframe of 0–180 min is shown to enhance the clarity of the figure. The actual measurement lasted 600 min.

This completely changes the picture of the energy balance of such a process. Instead of having plentiful energy left, a careful design of the heat recovery is essential in order to run this process without the need of external energy supply. In consequence, a diligent assessment is necessary to evaluate the feasibility of hydrothermal carbonization compared to other thermochemical processes dependent on the type of biomass available.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.biortech.2011.05.016](https://doi.org/10.1016/j.biortech.2011.05.016).

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